

SrRuO₃ Perovskite Based Compounds for
Supercapacitors:
Synthesis, Structure, and Electrochemical Performance
M. Wohlfahrt-Mehrens, J. Schenk, H. Dittrich,
P. Axmann, J. Garche
Center for Solar Energy and Hydrogen Research (ZSW)
Division for Electrochemical Energy Storage and
Energy Conversion
Helmholtzstrasse 8
D-89081 Ulm

Among the oxide materials for application in supercapacitors ruthenium oxides have achieved much attention [1-4], due to their high pseudocapacitance. Up to 500 F/g [5] or 720 F/g [6] are reported for amorphous water containing ruthenium oxides.

Ruthenates based on perovskite structure of the general formula ABO₃ containing ruthenium on the B position have been shown to exhibit pseudocapacitance behavior [7-8]. These materials also show metallic conductivity and are stable in aqueous alkaline electrolytes. Ruthenates with perovskite type structure offer a wide field for chemical modification by modifying the A and B site with foreign metals. The specific capacity as well as the stability window are strongly affected by dopands. Replacing up to 20 mole% strontium by lanthanum leads to an increase of the specific capacity and an extension of stability window about 0.1 V. On the other hand iron or cobalt substitution on the B-site reduces the stability range and has no beneficial effect on capacity, whereas doping by manganese increases the capacity without affecting the stability.

The aim of the work is increasing the capacity and reducing the amount of ruthenium by

- Increase of proton mobility in the perovskite structure
- Creating more additional free structure volume for the transport of counter ions during charge and discharge
- Increase of capacity by increasing Ru³⁺ content
- Built in of other redox components
- Increase of surface by preparation process

Therefore we have prepared a family of manganese mixed doped perovskites La_xSr_{1-x}Ru_{1-y}Mn_yO₃. These materials are formed by using a direct pyrolysis route. The precursor is an aqueous solution of ruthenium chloride, metal nitrates and strontium nitrate well in excess. This solution is pyrolysed at temperatures about 500 – 750 °C. The samples usually contain the desired perovskite and large amounts of water soluble strontium chloride and its hydrates. After removing these phases by washing with distilled water very porous samples of perovskites are obtained. The pseudocapacitance can be increased by doping up to about 20 % of lanthanum and manganese. Higher amounts of dopands leads to phase separation and decreased stability window. More detailed results concerning synthesis conditions, structure and electrochemical behavior of mixed doped strontium ruthenates will be presented.

REFERENCES

- [1] B. Conway, J. Electrochem. Soc. 138 (1991) 1539
- [2] M. Goodwin, Proceedings of the 6th International Seminar on Double Layer Capacitors and Similar

- Energy Storage Devices, Deerfield Beach, USA, Florida (1996)
- [3] S. Trasatti, P. Kurzweil, Plat. Met. Rev. 38 (2) (1994) 46
- [4] J.E. Oxley, Proceedings of 34th International Power Sources Symposium, June (1990) 25-28 Cherry Hill, NJ, USA
- [5] W. D. Ryden, A. W. Lawson, C.C. Sartain, Phys. Lett. 26A (1968) 209
- [6] P. Kurzweil, O. Schmid, A. Löffler, A. Koch, Proceedings of the 7th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, USA, Florida (1997)
- [7] P.M. Wilde, T.J. Guther, R. Oesten, J. Garche, J. Electroanalytical Chemistry 461 (1999) 154
- [8] T.J. Guther, R. Oesten, J. Garche, in F.M. Delnick, D. Ingersoll, X. Andrieu, K. Naoi (Eds.), Electrochemical Capacitors II, The Electrochemical Society Proceedings Series, vol. PV, Pennington, USA, NJ (1997) 16

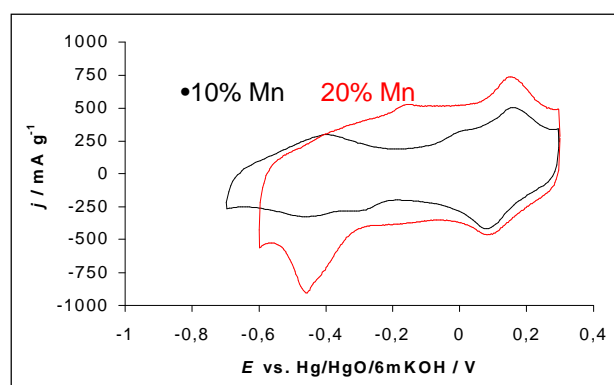


Figure 1: Cyclic voltammogram of two manganese doped strontium ruthenates SrRu_{1-x}Mn_xO₃ with x = 0,1; 0,2, scan rate 20 mV/s

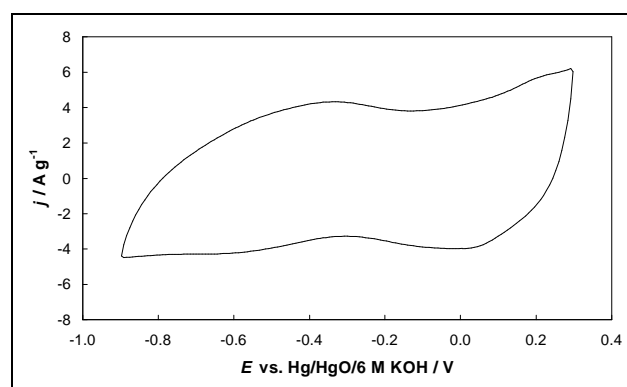


Figure 2: Cyclic voltammogram of La_{0.2}Sr_{0.8}RuO₃, scan rate 20 mV/s